



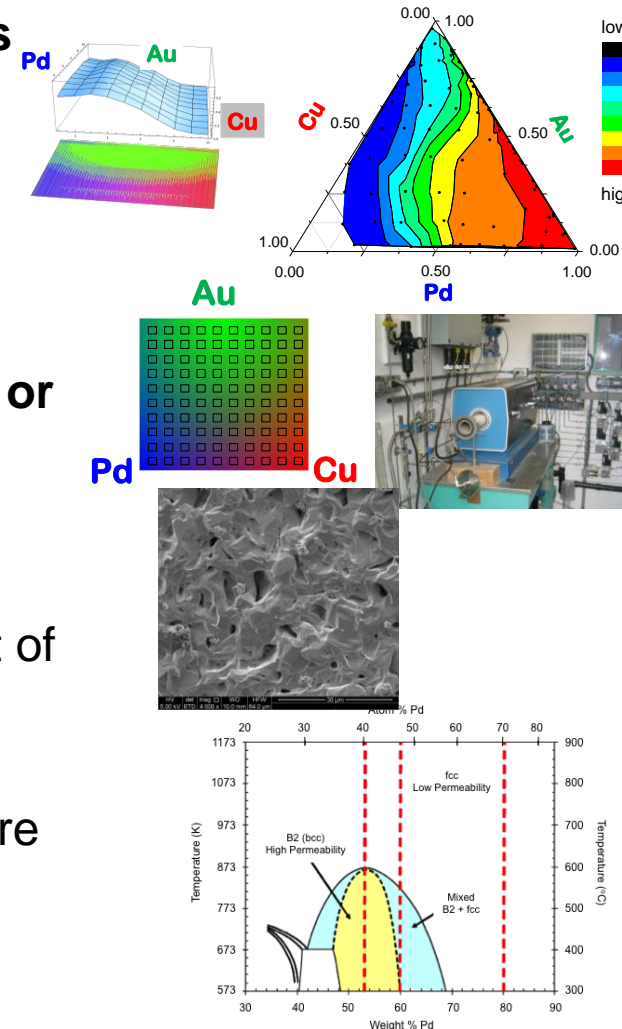
Fuels FWP

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Technical Coordinator

Fuels FWP Overview

Fuels Team Goals:

- Develop more rugged materials (i.e. catalysts, H₂-enrichment), and identify engineering opportunities to enhance process efficiency (i.e. reactor design) while overcoming thermodynamic limitations (i.e. process intensification).
- Explore materials and methods for advancing the conversion process for fossil gas components, whether to create fuels, chemicals and feedstocks, or power. The scope explores catalysis, separation, reactor design, and performance assessment.
- Focus:
 - Provide data needed to fully understand the impact of syngas environments on relevant hydrogen separation materials
 - Engineer membranes tailored for operation in severe environments of syngas conversion
 - Develop strategies to improve C1 conversion to useful products, such as BTEX



Challenges

- **Developing contaminant-tolerant materials for hydrogen separation in energy conversion systems**
 - Requirements:
 - Long lifetime
 - Resistance to contaminants (H_2S , As, Se, etc.)
 - Hydrogen permeance
- **Developing materials for conversion of fossil-based gases into value-added materials and feedstocks**
 - Requirements:
 - Long lifetime
 - Coke resistance
 - Conversion activity
- **Merging materials research with separation protocols to develop process intensification strategies for gas conversion**
 - Advantages:
 - Overcome thermodynamically limited reactions

Separation Materials Development

- **Goal:**

Combine experimental testing with targeted computational approaches to develop separation materials that have the ability to:

- Resist corrosion in contaminated environments
- Maintain activity for hydrogen dissociation and permeation
- Be as cost-effective as possible

- **Significant Issues:**

- **Poisoning**

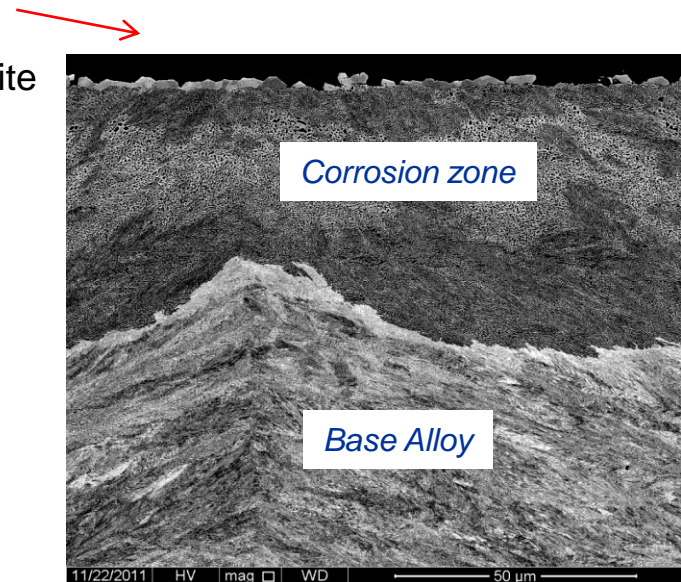
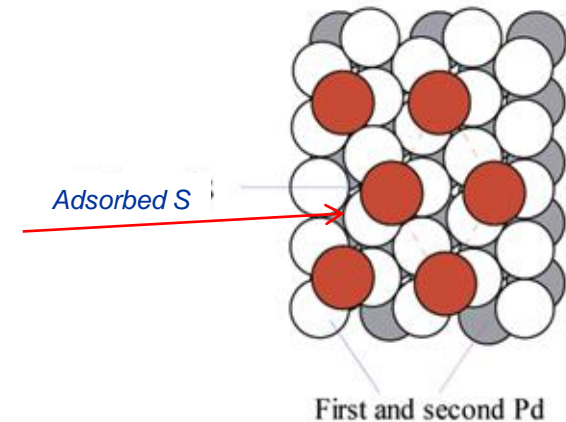
- Impurity atoms adsorbed on top atomic monolayer blocking sites for H_2 dissociation

- **Corrosion**

- Impurity elements reacting with one or more constituent elements in the membrane alloy forming a product(s) of a finite thickness on the surface

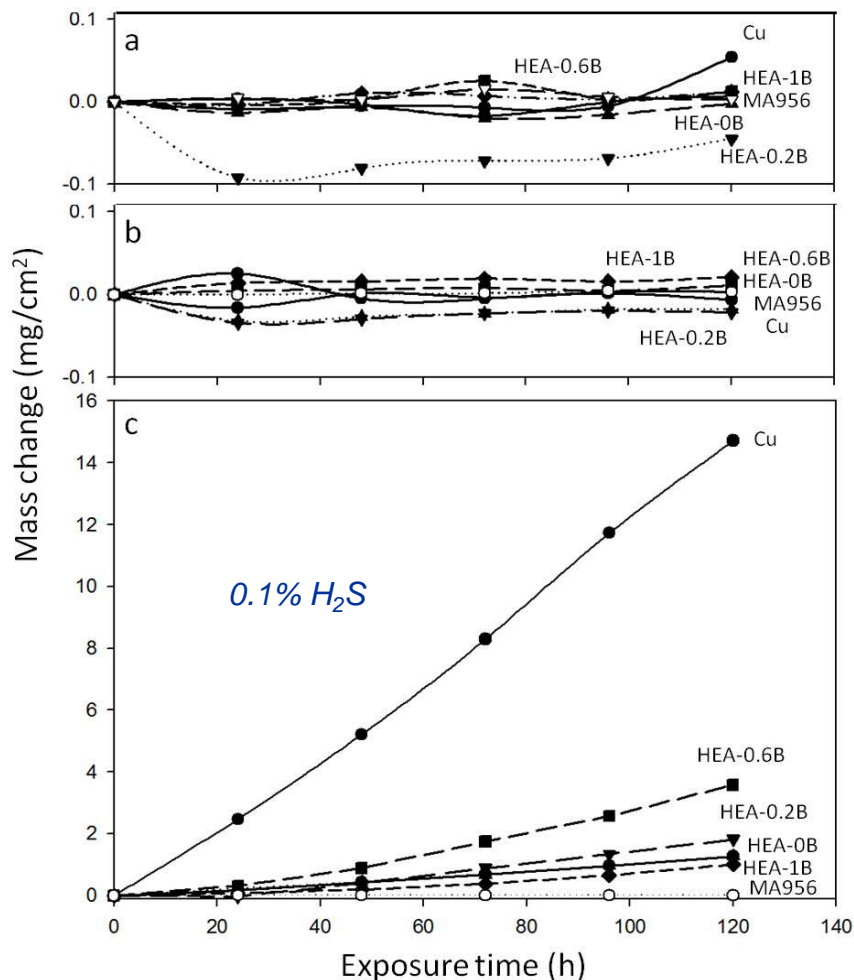
- **Testing:**

- Coupon exposure tests to determine stability of material in contaminated environments
 - Thin film reactivity testing across compositional space
 - Hydrogen permeability testing



Separation Materials Development

Exposure Testing of Alloys – mass change experiments



0% H₂S

No significant corrosion of high-entropy alloys was detected at 500 C in syngas containing 0 and 0.01% H₂S

0.01% H₂S

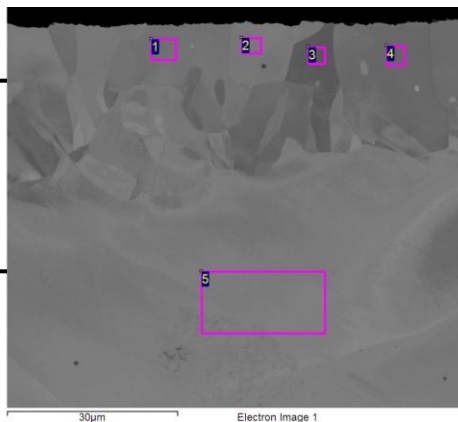
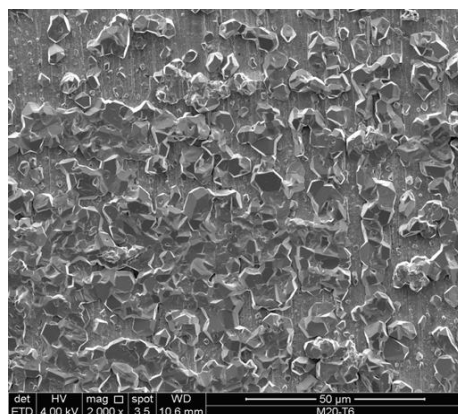
Significant corrosion of these alloys was observed in syngas containing 0.1 and 1% H₂S.

Separation Materials Development

Post-exposure Characterization of Membrane Alloys Exposed to Simulated Syngas with 0.1% and 1% H₂S at 500 C

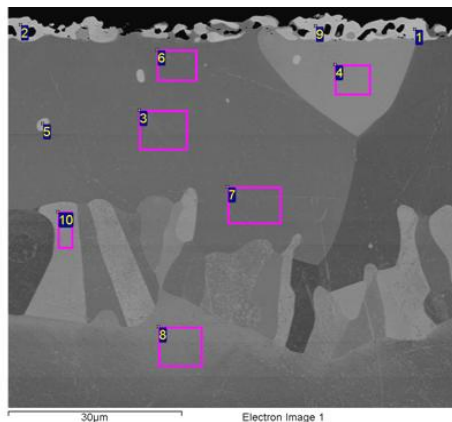
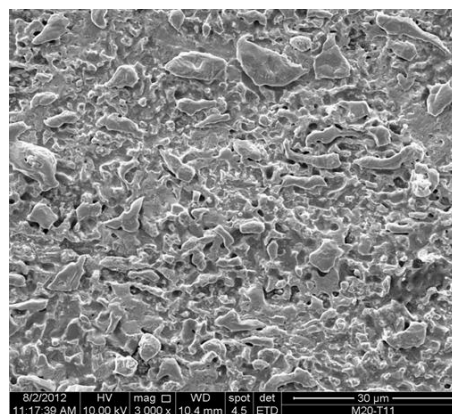


0.1% H₂S



Spectrum	S	Cu	Pd
1	2.1	52.4	45.5
2	2.2	52.4	45.5
3	1.9	52.6	45.5
4	1.9	52.2	45.8
5		53.4	46.6

1% H₂S



Spectrum	S	Cu	Pd
1	21.3	10.6	68.1
2	21.4	10.6	68.0
3	2.6	50.3	47.1
4	2.6	52.4	45.0
5	20.6	14.0	65.4
6	2.5	51.8	45.7
7	2.5	50.8	46.7
8		51.2	48.8
9	21.0	12.7	66.4
10		49.6	50.4

Separation Materials Developments

- **PdCu membrane materials offer some advantage over pure Pd materials, but binary alloys probably not the solution**
- **Multi-component alloys must be explored – high entropy alloys (5 or more metals combined at roughly equal proportions) may offer improved stability**
 - In general, the $\text{CoCrCuFeNiAl}_{0.5}\text{B}_x$ high-entropy alloys are shown to be stable in syngas containing 100 ppm H_2S at 500°C.
 - Our study suggests that these alloys may be stable at higher H_2S levels if their composition is modified by lowering or eliminating Cu.
 - Flux data is needed to determine whether these alloys can potentially be used as H_2 separation membranes.

Separation Materials Development

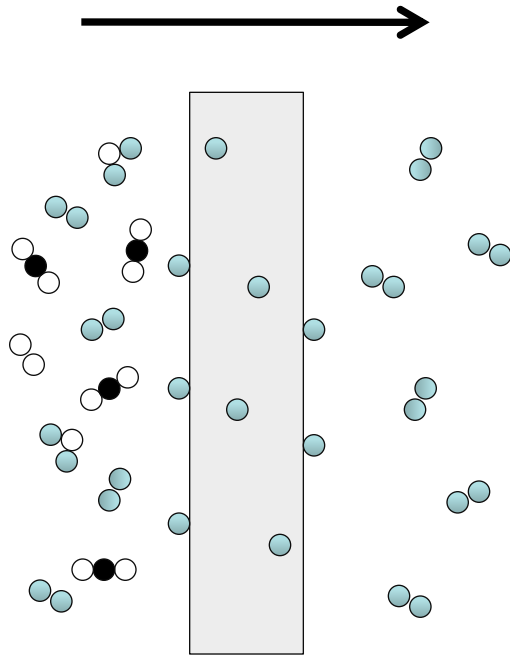
Multi-component Alloy System Overview:

- Fundamental understanding of the interaction of H_2 and H_2S with Pd alloy surfaces provides a basis for rational design of membrane systems that deliver high permeability and resistance to deactivation minor components
- High-throughput sample alloy libraries for the study of alloys across broad and complex composition and structure space
 - Characterization of microstructure and electronic structure across Cu_xPd_{1-x} composition space
 - Correlation between H_2 - D_2 exchange kinetic parameters and electronic structure across Cu_xPd_{1-x} composition space
 - Application of these tools across 3-component systems

Task 2.1.3 Accomplishments

Engineered Catalytic Surfaces

H₂ transport through Pd-alloy membranes



Recovery of ultrapure H₂ from products of coal gasification:

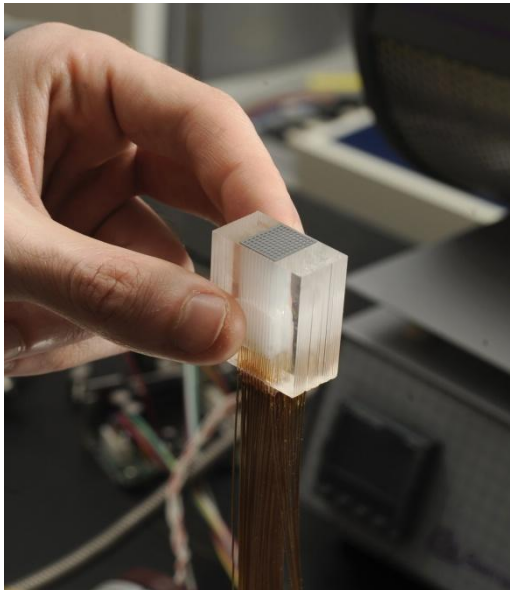
- Dissociative adsorption of H₂
- Diffusion of H-atoms through bulk
- Exposure to H₂S can disrupt either step

Alloys, i.e., PdCu, PdAu, PdAg can improve resistance to deactivation by H₂S and improve structural robustness

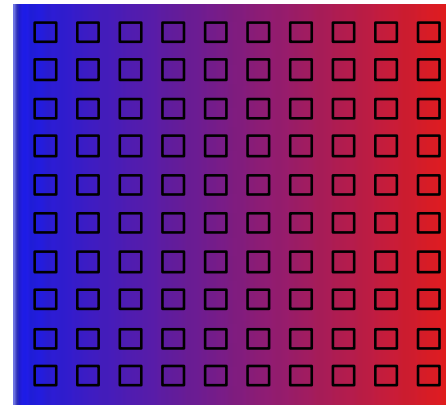
Task 2.1.3 Accomplishments

Engineered Catalytic Surfaces

Characterization of H_2 dissociation activity across composition space



Unique multi-channel micro reactor (provisional patent application) enables measurement of CSAF reactivity at 100 discrete locations

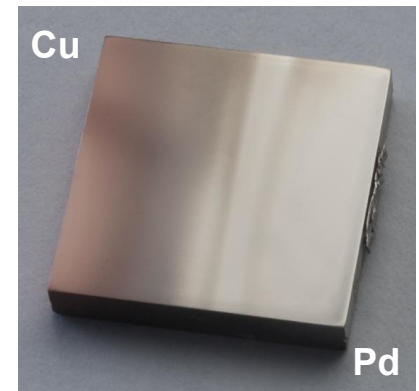
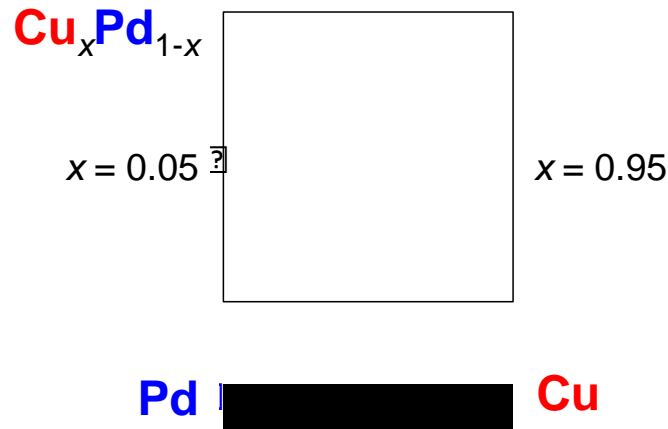
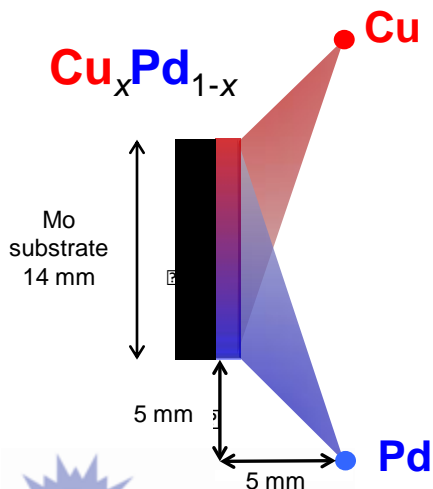


Task 2.1.3 Accomplishments

Engineered Catalytic Surfaces

The multicomponent materials challenge

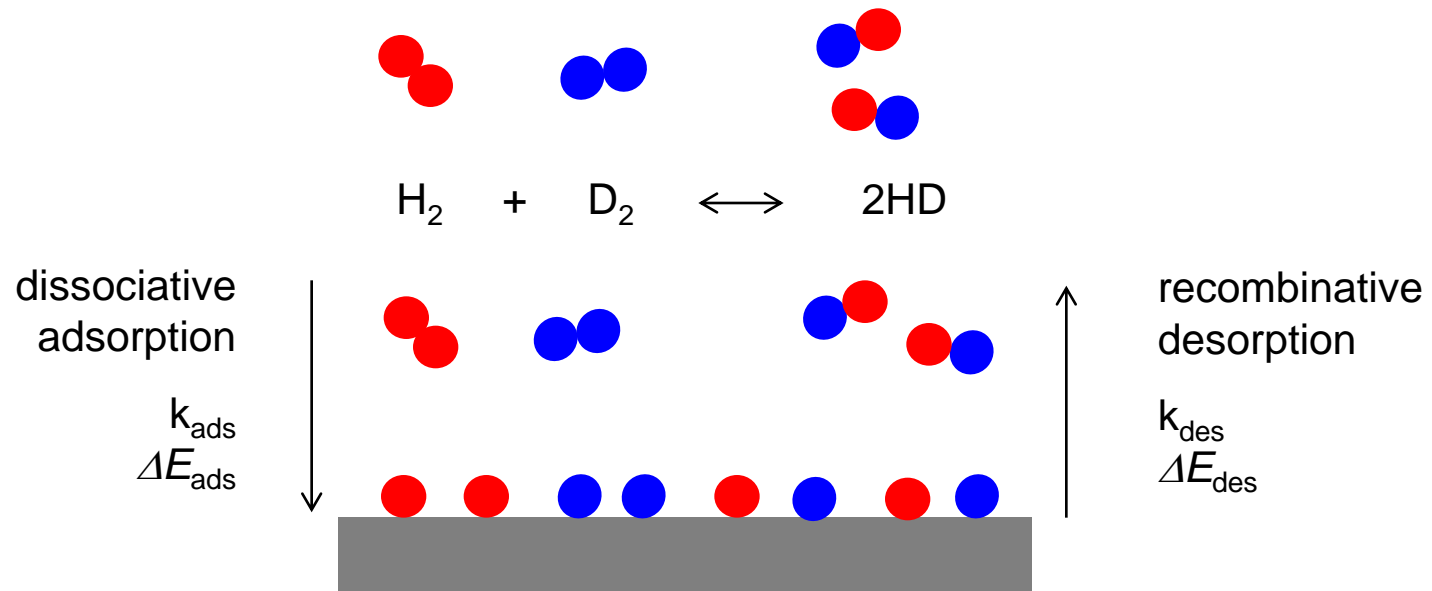
- **Challenge:**
 - Explore broad alloy composition space for identification of optimal compositions AND fundamental understanding (a basis for “rational design” that can be applied to other applications)
- **Approach:**
 - Composition spread alloy film (CSAF) libraries for rapid characterization of materials properties and functional properties across composition space



Task 2.1.3 Accomplishments

Engineered Catalytic Surfaces

Characterization of H_2 dissociation activity using H_2 - D_2 exchange



Which compositions are most active for dissociation? (optimization)

Why are those compositions the most active? (basic understanding for rational design)

Separation Materials Development

Bulk Hydrogen Transport Using Tubular Reactors

- **Purpose: Study bulk transport characteristics of alloys designed to be resistant to syngas impurities while maintaining flux**
 - Performance testing using HPTR and LPTRs
 - Characterization via XRD and SEM/EDS



Capabilities:

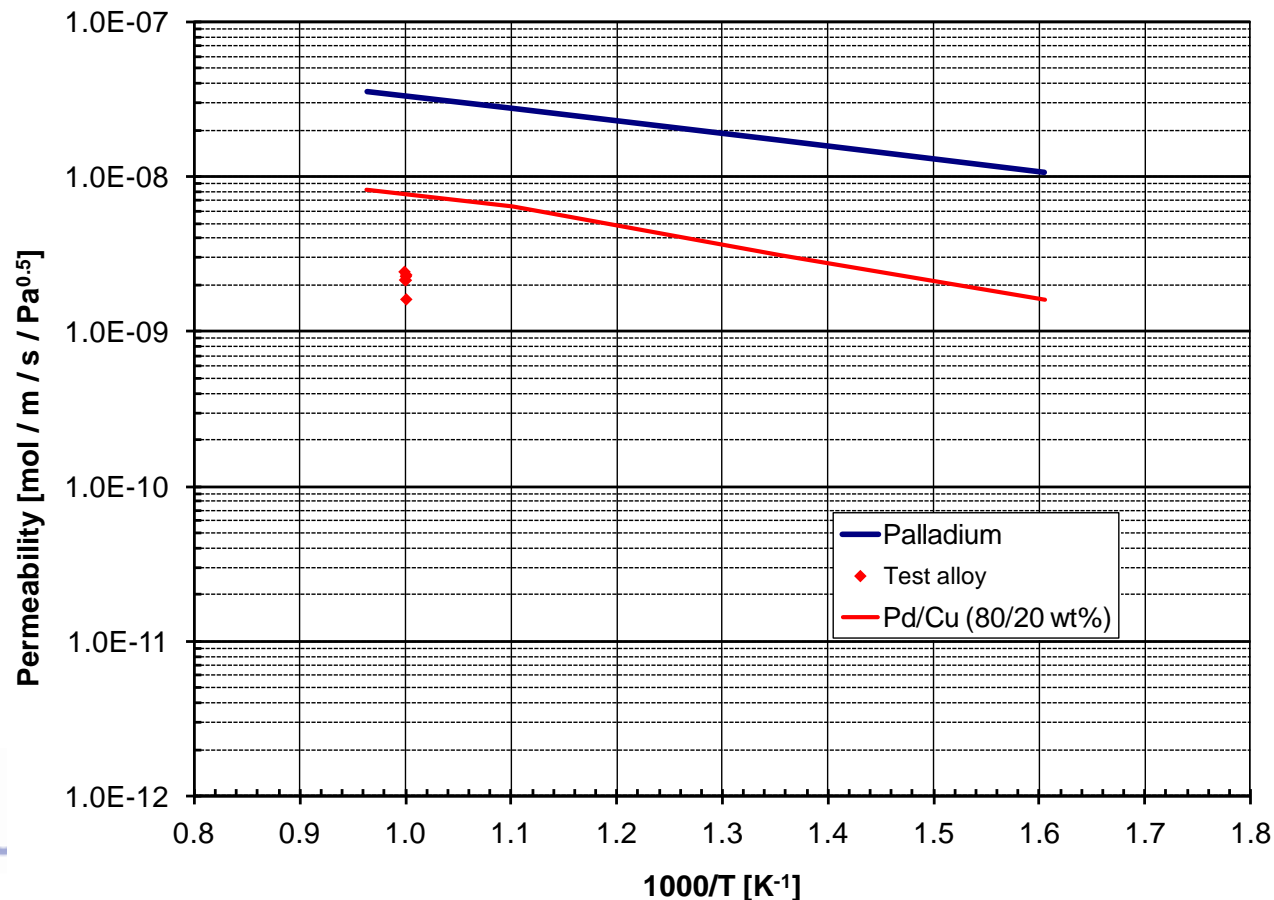
- Temperatures up to 900 °C
- Pressures up to 500 psig
- Flows up to 20 slpm
- Gas inputs:
 - CO₂
 - H₂
 - He
 - CO
 - H₂S

- **Alloy constituents:**

- Primarily Pd-based alloys with additives to modify surface characteristics
 - Pd-Cu ternaries, Pd-Au-Ag and Pd-Cu-Au alloy – S resistance
 - Non-Pd alloys – corrosion resistance

Membrane Test Units and Data

- **Purpose:** Provide actual performance data for membrane foils under conditions consistent with their application
 - 5 μm thick 80 wt% Pd-Cu
 - 100% H_2 , 725°C, feed pressure 0 to failure



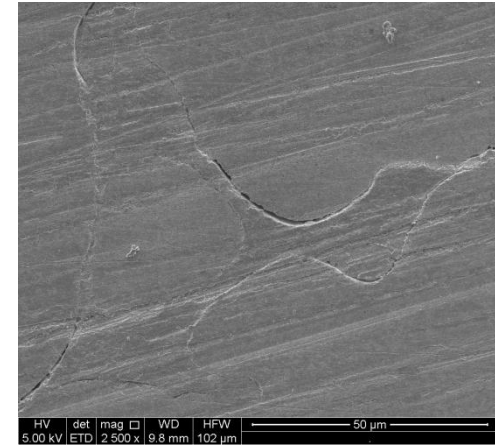
Post-test Membrane Evaluation

Use surface analysis techniques to examine exposed surfaces and link structure to performance

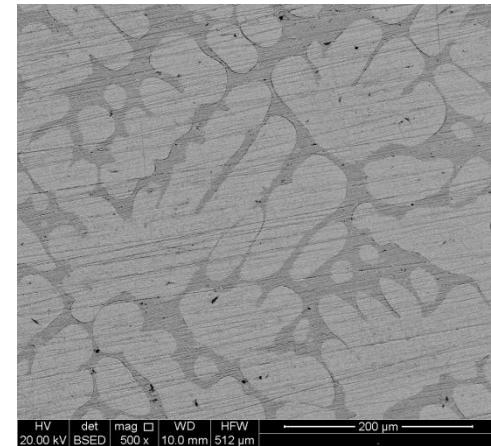
Analysis of 500°C failed membrane



Optical image showing mechanical stress crack (FOV=2mm)



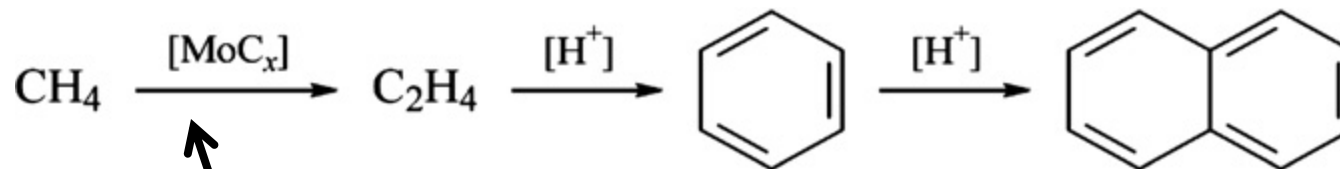
Secondary electron SEM image showing mechanical stress cracks at grain boundaries



Backscattered SEM image intergrown discrete alloy phases

Catalyst Development

Conversion of Gas Components



Mo/H-ZSM-5 mostly studied catalyst

MoC_x

Perform the dehydrogenation and coupling of methane to ethylene

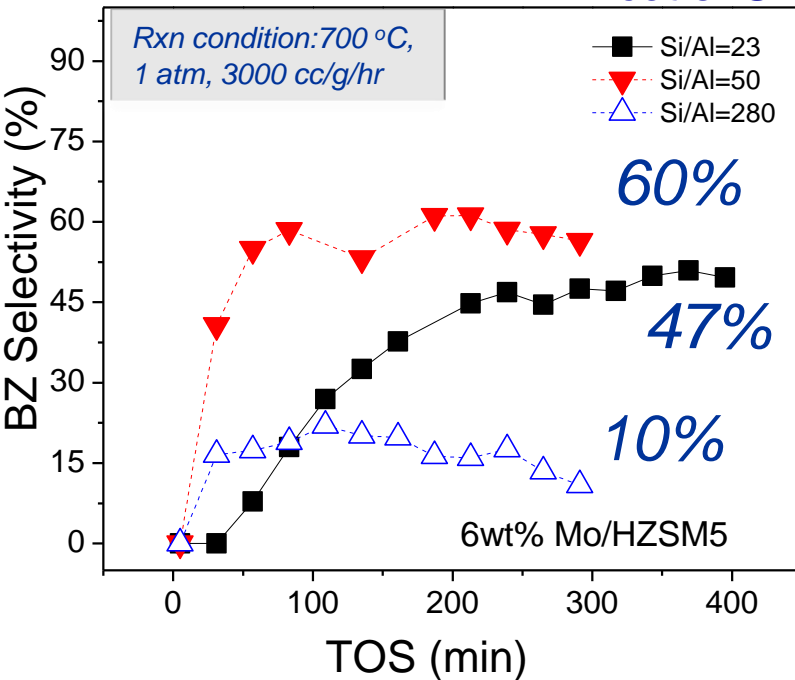
H-ZSM-5 $[\text{H}^+]$

- Provide Brønsted acidic sites
 - *Anchoring points for the molybdenum inside the channels of the ZSM-5*
 - Perform the ethylene oligomerization and ring closure reaction

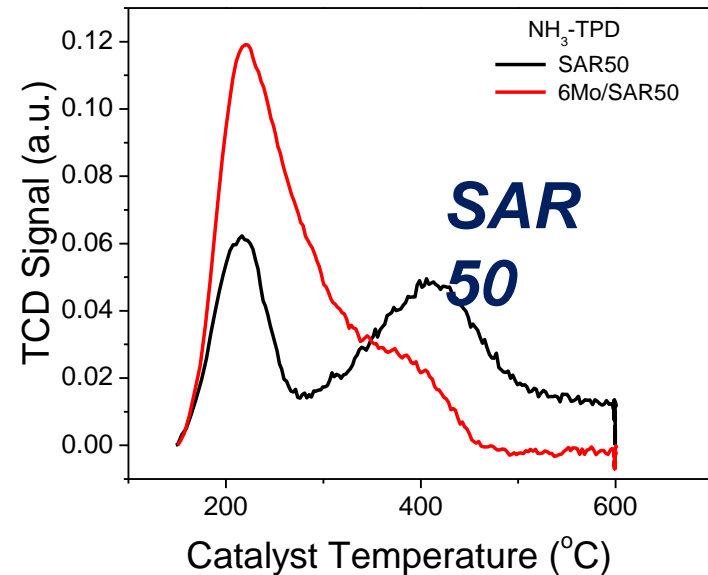
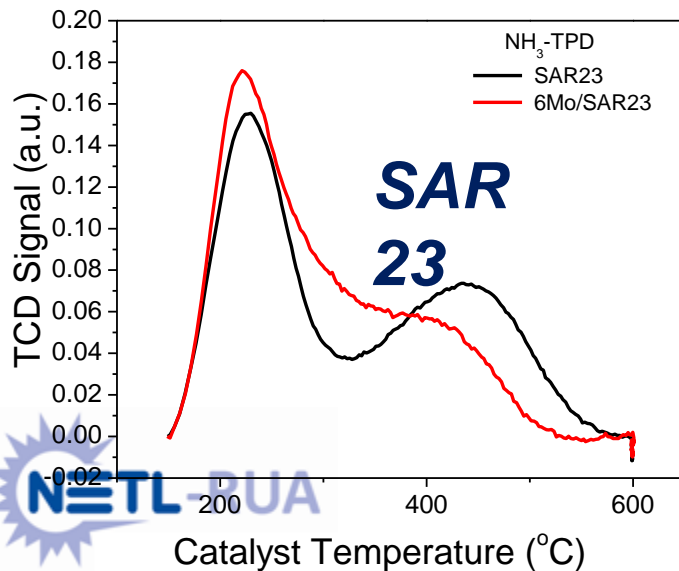
- **Barriers**
- Low methane conversion and product yields
- Long-term catalyst stability and activity
- Regeneration of deactivated catalysts

Catalyst Development

Effect of Si to Al Ratio (SAR) in ZSM-5



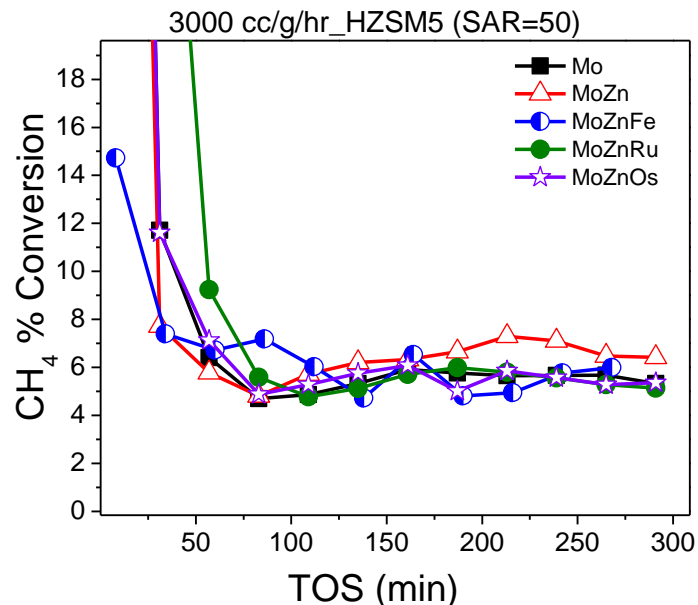
- Three Si-to Al ratio (SAR) – 23, 50, and 280
- SAR 50 (0-200min)
 - Highest benzene conversion
 - best balance between Bronsted acid sites and Mo catalyst distribution (co-existence)
- Acid sites decrease after loading of Mo indicating its migration inside zeolite pores



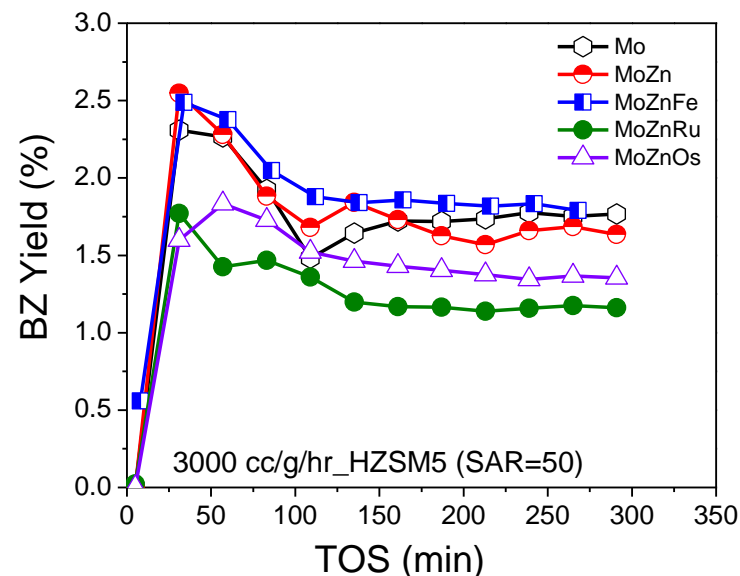
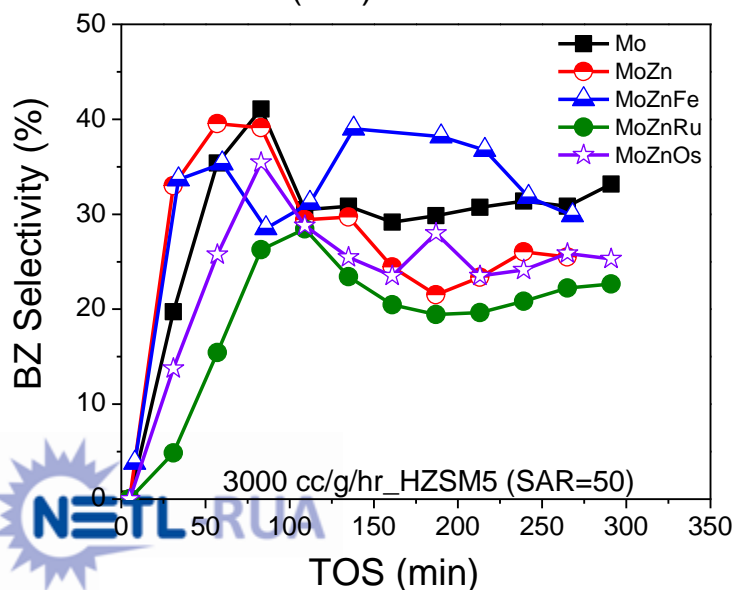
Catalyst Development

Results from MoZnM (M=Fe, Ru, Os)/H-ZSM5

700 °C, 1 atm, 3000 cc/g/h



- Initial methane conversion (<60min) is in this order: MoZn (5.7%)<Mo (6.4%)< MoZnFe(6.7%)<MoZnOs(7.1%)<MoZnRu(9.2%)
- After 300 min methane conversion become similar due to coke deposition on the catalyst
- Mo shows a higher benzene (BZ) selectivity compared to other metal added after 300min except for MoZnFe (TOS 150 to 250min) but it starts to deactivate

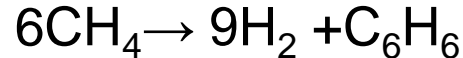


Process Development

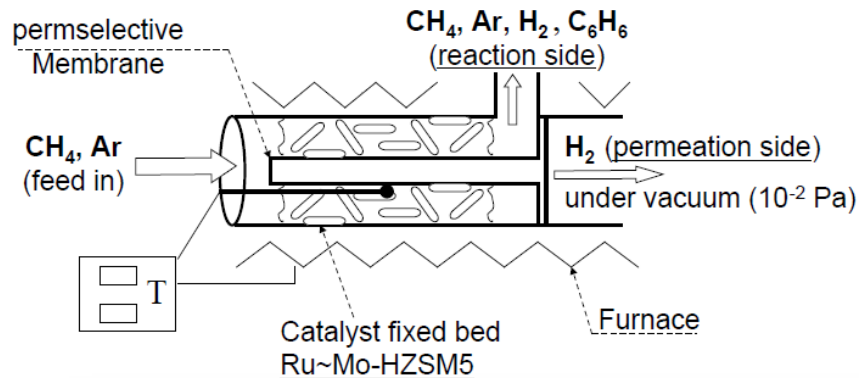
Process Intensification Opportunities

- Methane-to-aromatics reaction is amenable to enhancement by membrane reactor systems
- Primary obstacle appears to be formation of coke during reaction
- Methane DHA is thermodynamically limited to ~15% yield
- This limit can only be broken via reaction engineering measures, such as the use of catalytic membrane reactors for H₂ removal
- However, H₂ removal will further accelerate existing coking issues for the current state-of-the-art Mo/H-ZSM5 catalyst

Methane to Aromatics (Dehydroaromatization = DHA)

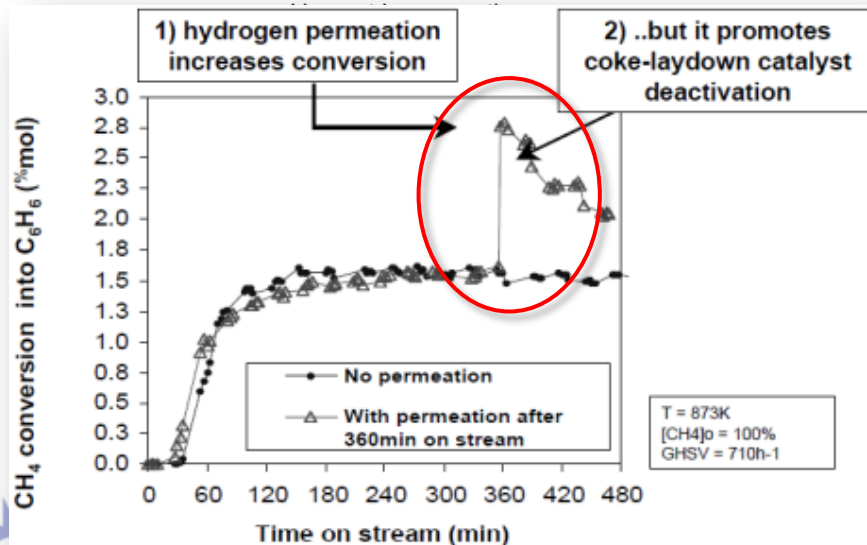
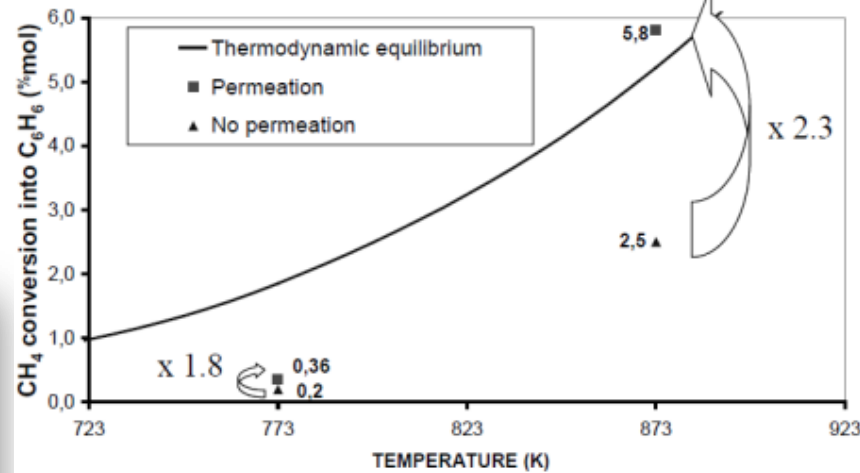


Methane DHA is thermodynamically limited to ~15% yield



Experimental Conditions

P permeation side = 0,2 Pa P reaction side = 101 kPa
G.H.S.V. = 350-400 h⁻¹ CH4 feed conc. = 100%



Improvements in reaction
Catalyst lifetime (resistance to coking)
Product removal strategies

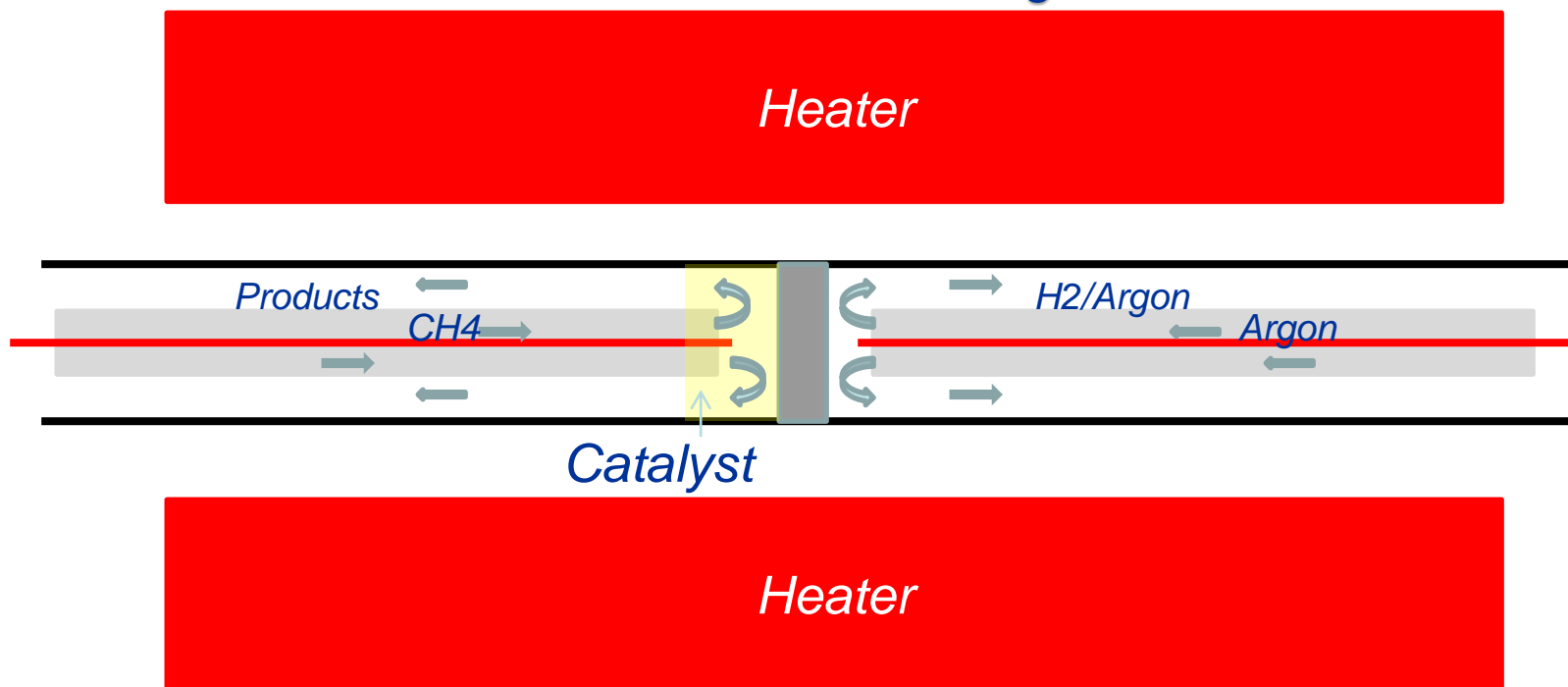
Process Intensification Opportunities:

C1 Conversion

- **Goal:**
 - Demonstrate improved methane to BTX conversions by employing a membrane reactor
- **Currently low conversions, ~15% maximum**
- **Membrane reactor philosophy:**
 - Benzene production, $6\text{CH}_4 \leftrightarrow \text{C}_6\text{H}_6 + 9\text{H}_2$ is pressure limited (6 gas molecules producing 10 gas molecules)
 - Membrane reactor can be used to remove H_2 which can shift equilibrium to benzene production and allow for a higher pressure process

Process Intensification

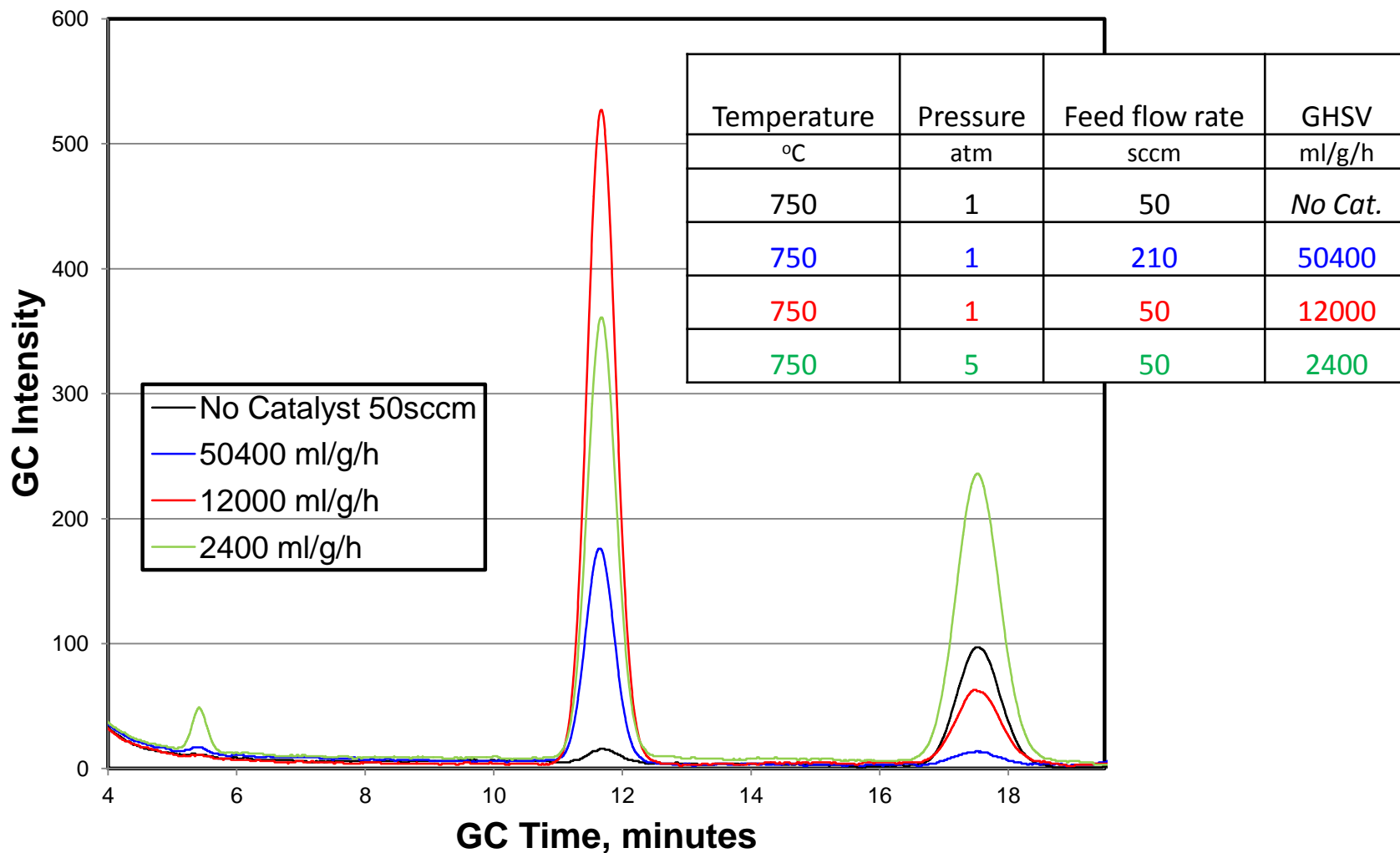
C1 Conversion Testing



Conditions:

- 100 μm thick, 16.2 mm dia., Pd membrane
- 750 °C
- 1-5 atm.
- 0.25 g 3% Mo, H-ZSM5, SAR 50
- Feed 50-210 sccm CH₄

C1 Conversion Products

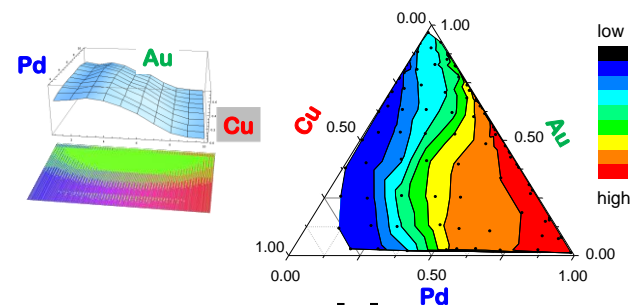
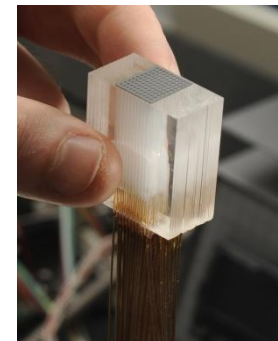
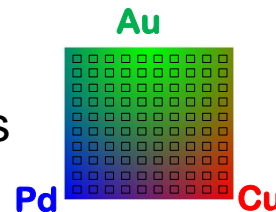


Product peaks at ~11.5 and 17.5 min. increased with the addition of catalyst and the decrease in space velocity

Progress Achieved

- **Development of tools for rapid screening of activity on binary and ternary thin films**

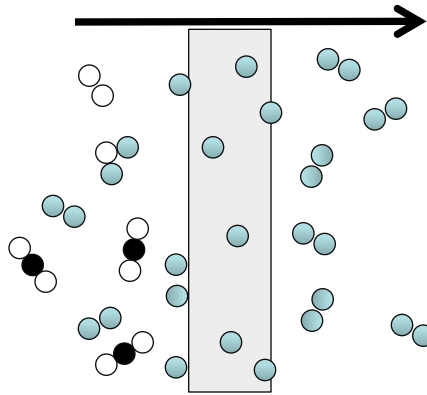
- Alloys, i.e., PdCu, PdCuAu can improve resistance to deactivation by H_2S and improve structural robustness
- Composition spread alloy film (CSAF) libraries and multichannel microreactor allow rapid characterization of materials properties and functional properties across composition space
- Explore broad alloy composition space for identification of optimal compositions AND fundamental understanding (a basis for “rational design” that can be applied to other applications)



- **PdCuX alloys [$\text{Cu}_{50}\text{Pd}_{44}\text{Mg}_6$ and $\text{Cu}_{50}\text{Pd}_{44}\text{Al}_6$] have comparable corrosion resistance to $\text{Cu}_{50}\text{Pd}_{50}$ in gas containing up to 1000 ppm H_2S**
- **Exposure of Pd alloys to “real syngas” revealed that additional contaminants (As, Se) may also be detrimental**

Importance of Successes

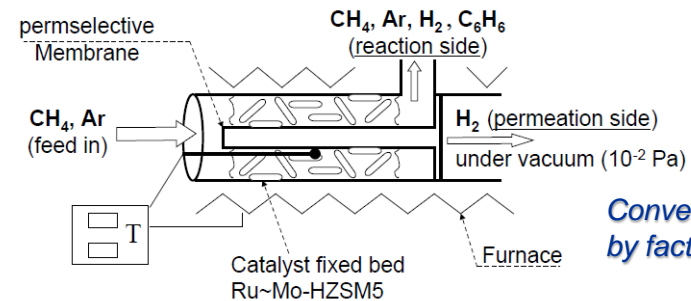
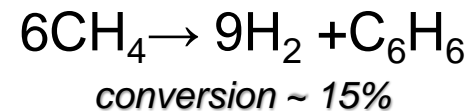
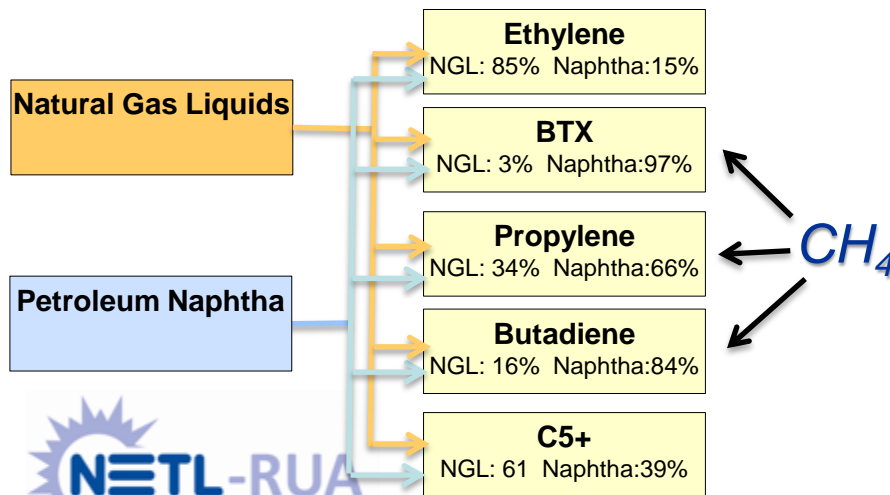
- Allows low cost, stable materials for separations and other processes to be developed



Recovery of ultrapure H₂ :

- Surface corrosion*: may alter dissociative adsorption of H₂
- Bulk corrosion*: may alter diffusion of H-atoms through bulk
- Exposure to H₂S /other contaminants can disrupt either step

- Allows abundant supply of gas to be used in important industrial processes and applications



Conversion increases by factor of >2

prepared by wet impregnation

Rival et al., 2nd Canadian-Korean joint workshop (2000)